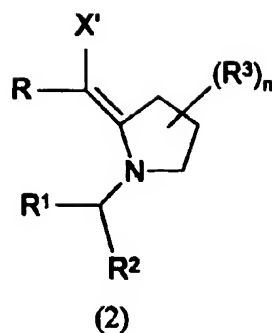


# Claims

**We Claim:**

1. A process for forming an intramolecular carbon-nitrogen bond which comprises reacting an  $sp^2$  hybridized carbon radical moiety with an azomethine moiety in the presence of a hydrogen atom donor, wherein said azomethine moiety possesses at least one radical stabilizing group, and the azomethine carbon is in the ketone oxidation state or higher.
2. The process of claim 1, wherein the azomethine carbon is in the ketone oxidation state.
3. The process of claim 1, wherein the azomethine carbon is bonded by groups selected from hydrocarbyl, substituted hydrocarbyl, aryl, and heteroaryl, provided that the atom bonded between such groups and the azomethine carbon will be other than a heteroatom.
4. The process of claim 1, wherein the azomethine carbon is bonded to at least one group selected from the group consisting of phenyl, vinyl, trifluormethyl, and carbonyl.
5. The process of claim 1, wherein the hydrogen atom donor is selected from organostannane hydrides, organosilyl silanes, organogermanium hydrides, 1,4-cyclohexadiene,  $\gamma$ -terpinene, thiols, and selenols.
6. The process of claim 5, wherein the organostannane is a compound of the Formula  $(X')_3Sn-H$ , wherein  $X'$  is a group selected from  $C_1-C_6$  alkyl, aryl, or a fluororous derivative thereof.
7. The process of claim 6, wherein the compound of the Formula a  $(X')_3Sn-H$  is tri-n-butyltin hydride.
8. The process of claim 1, wherein said process is applied to an array of compounds comprising an azomethine moiety to provide a library of compounds comprising a pyrrolidine and/or indoline subunit.
9. The process of claim 1, wherein said process is conducted on a solid support.
10. A process for preparing a compound of Formula (2)

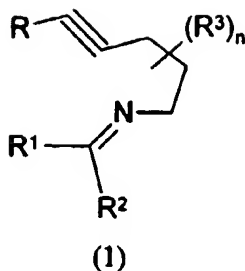


wherein each  $R$  is independently selected from the group consisting of hydrogen, hydrocarbyl, substituted hydrocarbyl, aryl, heteroaryl, substituted aryl, substituted heteroaryl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, heteroatom connected aryl, heteroatom connected heteroaryl, heteroatom connected substituted aryl, heteroatom connected substituted heteroaryl, a group of the formula  $-C(O)R^1$ , a group of the formula  $-O-R^1$ , a group of the formula  $-NHR^1$ , a group of the formula  $-N(R^1)_2$ , a group of the formula  $-Sn(R^1)_3$ , and a group of the formula  $-Si(R^1)_3$ ;

wherein the  $R^1$  and  $R^2$  groups are independently selected from the group consisting of aryl, heteroaryl, hydrocarbyl, substituted aryl, substituted heteroaryl, and substituted hydrocarbyl; provided that said groups are bonded via a carbon atom;

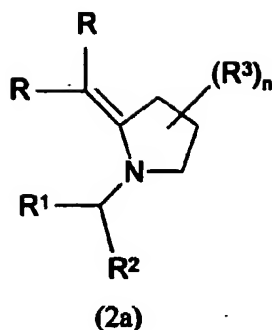
each  $R^3$  is independently selected from aryl; heteroaryl; hydrocarbyl; substituted aryl; substituted heteroaryl; substituted hydrocarbyl; heteroatom connected aryl; heteroatom connected hydrocarbyl; heteroatom connected substituted hydrocarbyl; heteroatom connected heteroaryl; heteroatom connected substituted aryl; halo; amino; cyano; hydroxy; carboxy; a group of the formula  $-C(O)O-C_1-C_8$  alkyl; a group of the formula  $-C(O)R^1$ ; a group of the formula  $-O-R^1$ ; a group of the formula  $-NHR^1$ ; a group of the formula  $-N(R^1)_2$ ;  $C_1-C_8$  alkoxy;  $C_1-C_8$  alkylthio; and oxo; or two  $R^3$  groups taken together can form a divalent hydrocarbyl, substituted hydrocarbyl, or be bonded directly to a heteroatom selected from oxygen, nitrogen, or sulfur; and  $n$  is from 0 to 6;

which comprises contacting a compound of Formula (1)



with a free radical initiator in the presence of a hydrogen atom donor, wherein R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and n are as defined above.

- R. 1.126
- 11  
~~18~~ 18. The process of claim 17, wherein the hydrogen atom donor is selected from organostannane hydrides, organosilyl silanes, organogermanium hydrides, 1,4-cyclohexadiene,  $\gamma$ -terpinene, thiols, and selenols.
- 12  
~~19~~ 19. The process of claim 18, wherein the organostannane is a compound of the Formula (X')<sub>3</sub>Sn-H, wherein X' is a group selected from C<sub>1</sub>-C<sub>6</sub> alkyl, aryl, or a fluorous derivative thereof.
- 13  
~~20~~ 20. The process of claim 17, wherein the compound of the Formula (X')<sub>3</sub>Sn-H is tri-n-butyltin hydride.
- 14  
~~21~~ 21. The process of claim 17, wherein the free radical initiator is selected from the group consisting of azonitriles and peroxides.
- 15  
~~22~~ 22. The process of claim 21, wherein the free radical initiator is 2,2'-azobisisobutyronitrile.
- 16  
~~23~~ 23. The process of claim 17, wherein the compound of Formula (1) is attached to a solid support.
- 17  
~~24~~ 24. A process for preparing compounds of the formula

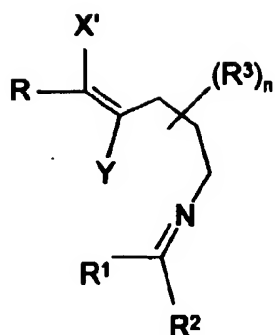


wherein each R is independently selected from the group consisting of hydrogen, hydrocarbyl, substituted hydrocarbyl, aryl, heteroaryl, substituted aryl, substituted heteroaryl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, heteroatom connected aryl, heteroatom connected heteroaryl, heteroatom connected substituted aryl, heteroatom connected substituted heteroaryl, a group of the formula  $-C(O)R^1$ , a group of the formula  $-O-R^1$ , a group of the formula  $-NHR^1$ , a group of the formula  $-N(R^1)_2$ , a group of the formula  $-Sn(R^1)_3$ , and a group of the formula  $-Si(R^1)_3$ ;

wherein the  $R^1$  and  $R^2$  groups are independently selected from the group consisting of aryl, heteroaryl, hydrocarbyl, substituted aryl, substituted heteroaryl, and substituted hydrocarbyl; provided that said groups are bonded via a carbon atom;

each  $R^3$  is independently selected from aryl; heteroaryl; hydrocarbyl; substituted aryl; substituted heteroaryl; substituted hydrocarbyl; heteroatom connected aryl; heteroatom connected hydrocarbyl; heteroatom connected substituted hydrocarbyl; heteroatom connected heteroaryl; heteroatom connected substituted aryl; amino; halo; cyano; hydroxy; carboxy; a group of the formula  $-C(O)O-C_1-C_8$  alkyl; a group of the formula  $-C(O)R^1$ ; a group of the formula  $-O-R^1$ ; a group of the formula  $-NHR^1$ ; a group of the formula  $-N(R^1)_2$ ;  $C_1-C_8$  alkoxy;  $C_1-C_8$  alkylthio; and oxo; or two  $R^3$  groups taken together can form a divalent hydrocarbyl, substituted hydrocarbyl, or be bonded directly to a heteroatom selected from oxygen, nitrogen, or sulfur; and n is 0, 1 or 2;

which comprises contacting a compound of the formula



with a free radical initiator in the presence of a hydrogen atom donor, wherein Y is a radical leaving group, and X' is selected from C<sub>1</sub>-C<sub>6</sub> alkyl, aryl, or a fluorous derivative thereof.

18

<sup>18</sup>25. The process of claim 24, wherein the hydrogen atom donor is selected from organostannane hydrides, organosilyl silanes, organogermanium hydrides, 1,4-cyclohexadiene,  $\gamma$ -terpinene, thiols, and selenols.

19

<sup>19</sup>26. The process of claim 25, wherein the organostannane is a compound of the Formula (X')<sub>3</sub>Sn-H, wherein X' is a group selected from C<sub>1</sub>-C<sub>6</sub> alkyl, aryl, or a fluorous derivative thereof.

20

<sup>20</sup>27. The process of claim 25, wherein the compound of the Formula (X')<sub>3</sub>Sn-H is tri-n-butyltin hydride.

21

<sup>21</sup>28. The process of claim 25, wherein the free radical initiator is selected from the group consisting of azonitriles and peroxides.

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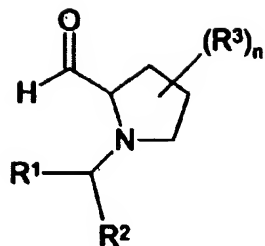
<sup>22</sup>29. The process of claim 28, wherein the free radical initiator is 2,2'-azobisisobutyronitrile.

23

<sup>23</sup>30. The process of claim 24, wherein the compound of Formula (1) is attached to a solid support.

24

<sup>24</sup>31. The process of claim 17 or 24, further comprising the steps:  
 a) epoxidation, followed by acid catalyzed rearrangement to afford an amino aldehyde, of the formula

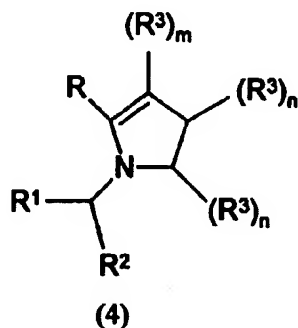


followed by

- (b) treatment of the resulting aldehyde with a suitable inorganic oxidizing agent,
- (c) followed by deprotection of the nitrogen to provide proline.

25

32. A process for preparing a compound of the Formula (4)

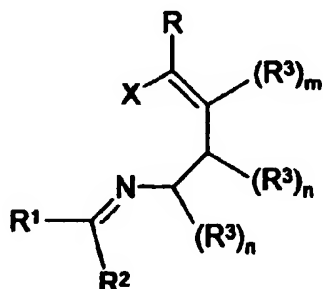


wherein each R is independently selected from the group consisting of hydrogen, hydrocarbyl, substituted hydrocarbyl, aryl, heteroaryl, substituted aryl, substituted heteroaryl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, heteroatom connected aryl, heteroatom connected heteroaryl, heteroatom connected substituted aryl, heteroatom connected substituted heteroaryl, a group of the formula  $-C(O)R^1$ , a group of the formula  $-O-R^1$ , a group of the formula  $-NHR^1$ , a group of the formula  $-N(R^1)_2$ , a group of the formula  $-Sn(R^1)_3$ , and a group of the formula  $-Si(R^1)_3$ ;

wherein the  $R^1$  and  $R^2$  groups are independently selected from the group consisting of aryl, heteroaryl, hydrocarbyl, substituted aryl, substituted heteroaryl, and substituted hydrocarbyl; provided that said groups are bonded via a carbon atom;

each  $R^3$  is independently selected from aryl; heteroaryl; hydrocarbyl; substituted aryl; substituted heteroaryl; substituted hydrocarbyl; heteroatom connected aryl; heteroatom connected hydrocarbyl; heteroatom connected substituted hydrocarbyl; heteroatom connected heteroaryl; heteroatom connected substituted aryl; amino; halo; cyano; hydroxy; carboxy; a group of the formula  $-C(O)O-C_1-C_8$  alkyl; a group of the formula  $-C(O)R^1$ ; a group of the formula  $-O-R^1$ ; a group of the formula  $-NHR^1$ ; a group of the formula  $-N(R^1)_2$ ;  $C_1-C_8$  alkoxy;  $C_1-C_8$  alkylthio; and oxo; or two  $R^3$  groups taken together can form a divalent hydrocarbyl, substituted hydrocarbyl, or be bonded directly to a heteroatom selected from oxygen, nitrogen, or sulfur; m is 0 or 1; and each n is 0, 1 or 2;

which comprises contacting a compound of the Formula (3)



(3)

wherein R,  $R^1$ ,  $R^2$ , and  $R^3$ , and n are as defined for Formula (4), and X is a halide, with a free radical initiator in the presence of a hydrogen atom donor.

26

33. The process of claim 32, wherein the hydrogen atom donor is selected from organostannane hydrides, organosilyl silanes, organogermanium hydrides, 1,4-cyclohexadiene,  $\gamma$ -terpinene, thiols, and selenols.

27

34. The process of claim 32, wherein the organostannane is a compound of the Formula  $(X')_3Sn-H$ , wherein  $X'$  is a group selected from  $C_1-C_8$  alkyl, aryl, or a fluoros derivative thereof.

28

35. The process of claim 32, wherein the compound of the Formula  $(X')_3Sn-H$  is tri-n-butyltin hydride.

29

36. The process of claim 32, wherein the free radical initiator is selected from the group consisting of azonitriles and peroxides.

30

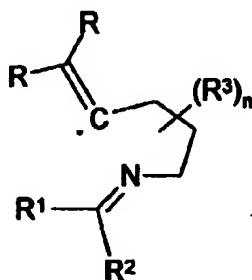
37. The process of claim 32, wherein the free radical initiator is 2,2'-azobisisobutyronitrile.

31

38. The process of claim 32, wherein the compound of Formula (3) is attached to a solid support.

32

39. A free radical intermediate of the Formula



wherein each R is independently selected from the group consisting of hydrogen, hydrocarbyl, substituted hydrocarbyl, aryl, heteroaryl, substituted aryl, substituted heteroaryl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, heteroatom connected aryl, heteroatom connected heteroaryl, heteroatom connected substituted aryl, heteroatom connected substituted heteroaryl, a group of the formula  $-C(O)R^1$ , a group of the formula  $-O-R^1$ , a group of the formula  $-NHR^1$ , a group of the formula  $-N(R^1)_2$ , a group of the formula  $-Sn(R^1)_3$ , and a group of the formula  $-Si(R^1)_3$ ;

wherein the  $R^1$  and  $R^2$  groups are independently selected from the group consisting of aryl, heteroaryl, hydrocarbyl, substituted aryl, substituted heteroaryl, and substituted hydrocarbyl; provided that said groups are bonded via a carbon atom;

each  $R^3$  is independently selected from aryl; heteroaryl; hydrocarbyl; substituted aryl; substituted heteroaryl; substituted hydrocarbyl; heteroatom connected aryl; heteroatom connected hydrocarbyl; heteroatom connected substituted hydrocarbyl; heteroatom connected heteroaryl;



heteroatom connected substituted aryl; amino; halo; cyano; hydroxy; carboxy; a group of the formula  $-C(O)O-C_1-C_n$  alkyl; a group of the formula  $-C(O)R^1$ ; a group of the formula  $-O-R^1$ ; a group of the formula  $-NHR^1$ ; a group of the formula  $-N(R^1)_2$ ;  $C_1-C_n$  alkoxy;  $C_1-C_n$  alkylthio; and oxo; or two  $R^3$  groups taken together can form a divalent hydrocarbyl, substituted hydrocarbyl, or be bonded directly to a heteroatom selected from oxygen, nitrogen, or sulfur; and  $n$  is from 0 to 6.

<sup>33</sup>  
40. The intermediate of claim 39, wherein  $R^1$  and  $R^2$  are selected from phenyl, trifluoromethyl, and  $C_1-C_n$  alkyl.

<sup>34</sup>  
41. The intermediate of claim 39, wherein  $n$  is 0.

<sup>35</sup>  
42. The intermediate of claim 39, wherein  $R^3$  is fluoro.

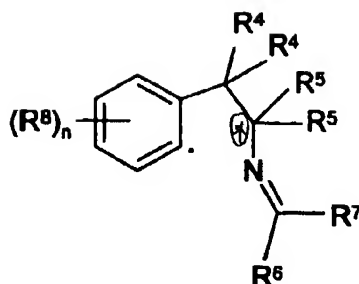
<sup>36</sup>  
43. A process for forming a carbon-nitrogen bond, wherein said carbon is part of an aryl or heteroaryl ring, which comprises reacting an aryl or heteroaryl radical moiety with an azomethine moiety in the presence of a hydrogen atom donor in an intramolecular reaction to form a fused ring system, wherein said azomethine moiety possesses at least one radical stabilizing group, and the azomethine carbon is in the ketone oxidation state or higher.

<sup>37</sup>  
44. The process of claim 43, wherein the hydrogen atom donor is selected from the group consisting of organostannane hydrides, organosilyl silanes, organogermanium hydrides, 1,4-cyclohexadiene,  $\gamma$ -terpinene, thiols, and selenols.

<sup>38</sup>  
45. The process of claim 44, wherein the organostannane is a compound of the Formula  $(X')_3Sn-H$ , wherein  $X'$  is a group selected from  $C_1-C_6$  alkyl, aryl, or flourous derivative thereof.

<sup>39</sup>  
46. The process of claim 45, wherein the compound of the Formula  $(X)_3Sn-H$  is tri- $n$ -butyltin hydride.

<sup>40</sup>  
47. The process of claim 43, wherein the aryl radical moiety and azomethine moiety are contained within a compound of the Formula



wherein each of the groups  $R^4$ ,  $R^5$ , and  $R^8$  are independently selected from hydrogen, aryl; heteroaryl; hydrocarbyl; substituted aryl; substituted heteroaryl; substituted hydrocarbyl; heteroatom connected aryl; heteroatom connected hydrocarbyl; heteroatom connected substituted hydrocarbyl; heteroatom connected heteroaryl; heteroatom connected substituted aryl; halo; amino; cyano; hydroxy; carboxy; a group of the formula  $-C(O)O-C_1-C_8$  alkyl; a group of the formula  $-C(O)R^1$ ; a group of the formula  $-O-R^1$ ; a group of the formula  $-NHR^1$ ; a group of the formula  $-N(R^1)_2$ ;  $C_1-C_8$  alkoxy;  $C_1-C_8$  alkylthio; or two of  $R^5$  and  $R^6$ , or two  $R^8$  groups taken together can form a divalent hydrocarbyl, substituted hydrocarbyl, or be bonded directly to a heteroatom selected from oxygen, nitrogen, or sulfur;

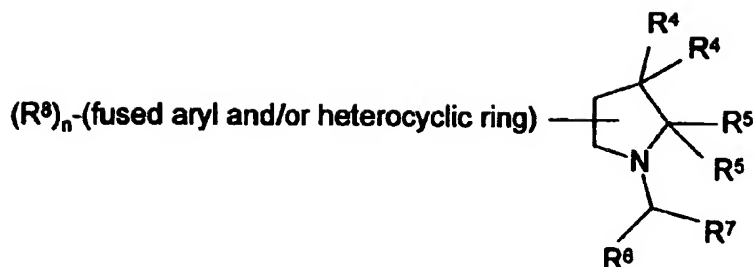
in addition, two  $R^4$  groups and/or two  $R^5$  groups can be taken together represent oxo;

$R^6$  and  $R^7$  are independently selected from aryl, heteroaryl, hydrocarbyl, substituted aryl, substituted heteroaryl, and substituted hydrocarbyl; provided that said groups are bonded via a carbon atom;

and  $n$  is from 0 to 4.

<sup>41</sup>  
~~48~~ The process of claim 43, wherein the azomethine moiety is attached to a solid support.

<sup>42</sup>  
~~49~~ A process for preparing compounds of the formula



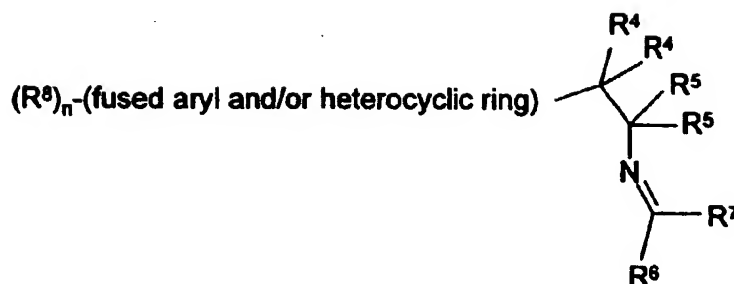
wherein each of the groups  $R^4$ ,  $R^5$ , and  $R^8$  are independently selected from hydrogen, aryl; heteroaryl; hydrocarbyl; substituted aryl; substituted heteroaryl; substituted hydrocarbyl; heteroatom connected aryl; heteroatom connected hydrocarbyl; heteroatom connected substituted hydrocarbyl; heteroatom connected heteroaryl; heteroatom connected substituted aryl; halo; amino; cyano; hydroxy; carboxy; a group of the formula  $-C(O)O-C_1-C_n$  alkyl; a group of the formula  $-C(O)R^1$ ; a group of the formula  $-O-R^1$ ; a group of the formula  $-NHR^1$ ; a group of the formula  $-N(R^1)_2$ ;  $C_1-C_n$  alkoxy;  $C_1-C_n$  alkylthio; or two of  $R^5$  and  $R^6$ , and/or two  $R^8$  groups taken together can form a divalent hydrocarbyl, substituted hydrocarbyl, or be bonded directly to a heteroatom selected from oxygen, nitrogen, or sulfur; and  $n$  is from 0 to a number equivalent to available sites on said fused aryl and/or heterocyclic ring;

in addition, two  $R^4$  groups and/or two  $R^5$  groups can be taken together represent oxo;

$R^6$  and  $R^7$  are independently selected from aryl, heteroaryl, hydrocarbyl, substituted aryl, substituted heteroaryl, and substituted hydrocarbyl; provided that said groups are bonded via a carbon atom;

and  $n$  is from 0 to 4;

which comprises contacting a compound of the formula



wherein said fused aryl and/or heterocyclic ring possesses a carbon alpha to its point of attachment capable of forming an  $sp^2$  hybridized carbon radical, said carbon substituted by a group Y, wherein Y is a radical leaving group;

with a free radical initiator in the presence of a hydrogen atom donor.

43

50. The process of claim 49, wherein the hydrogen atom donor is selected from the group consisting of organostannane hydrides, organosilyl silanes, organogermanium hydrides, 1,4-cyclohexadiene,  $\gamma$ -terpinene, thiols, and selenols.

44

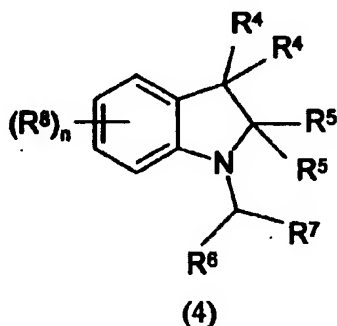
51. The process of claim 50, wherein the organostannane is a compound of the Formula  $(X')_3Sn-H$ , wherein  $X'$  is a group selected from  $C_1-C_6$  alkyl, aryl, or flourous derivative thereof.

45

52. The process of claim 51, wherein the compound of the Formula  $(X')_3Sn-H$  is tri-n-butyltin hydride.

46

53. A process for preparing a compound of Formula (4)



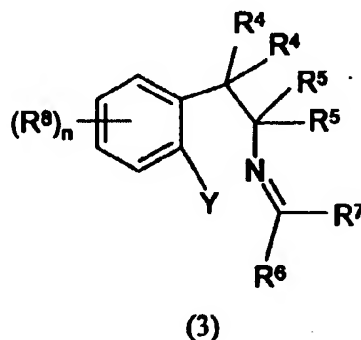
wherein each of the groups  $R^4$ ,  $R^5$ , and  $R^6$  are independently selected from hydrogen, aryl; heteroaryl; hydrocarbyl; substituted aryl; substituted heteroaryl; substituted hydrocarbyl; heteroatom connected aryl; heteroatom connected hydrocarbyl; heteroatom connected substituted hydrocarbyl; heteroatom connected heteroaryl; heteroatom connected substituted aryl; halo; amino; cyano; hydroxy; carboxy; a group of the formula  $-C(O)O-C_1-C_8$  alkyl; a group of the formula  $-C(O)R^1$ ; a group of the formula  $-O-R^1$ ; a group of the formula  $-NHR^1$ ; a group of the formula  $-N(R^1)_2$ ;  $C_1-C_8$  alkoxy;  $C_1-C_8$  alkylthio; or two of  $R^5$  and  $R^6$ , or two  $R^6$  groups taken together can form a divalent hydrocarbyl, substituted hydrocarbyl, or be bonded directly to a heteroatom selected from oxygen, nitrogen, or sulfur;

in addition, two  $R^4$  groups and/or two  $R^5$  groups can be taken together represent oxo;

$R^6$  and  $R^7$  are independently selected from aryl, heteroaryl, hydrocarbyl, substituted aryl, substituted heteroaryl, and substituted hydrocarbyl; provided that said groups are bonded via a carbon atom;

and n is from 0 to 4;

which comprises contacting a compound of Formula (3)



with a free radical initiator in the presence of a hydrogen atom donor, wherein Y is a radical leaving group.

<sup>47</sup>  
<sup>54</sup> The process of claim 53, wherein the hydrogen atom donor is selected from organostannane hydrides, organosilyl silanes, organogermanium hydrides, 1,4-cyclohexadiene,  $\gamma$ -terpinene, thiols, and selenols.

<sup>48</sup>  
<sup>55</sup> The process of claim 54, wherein the organostannane is a compound of the Formula  $(X')_3\text{Sn-H}$ , wherein  $X'$  is a group selected from  $C_1-C_6$  alkyl, aryl, or flourous derivative therof.

<sup>49</sup>  
<sup>56</sup> The process of claim 55, wherein the compound of the Formula  $(X)_3\text{Sn-H}$  is tri-n-butyltin hydride.

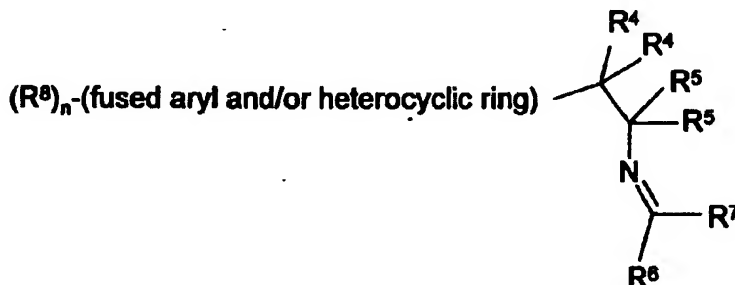
<sup>50</sup>  
<sup>57</sup> The process of claim 53, wherein the free radical initiator is selected from the group consisting of azonitriles and peroxides

<sup>51</sup>  
<sup>58</sup> The process of claim 57, wherein the free radical intitator is comprised of 2,2'-azobisisobutyronitrile.

<sup>52</sup>  
<sup>59</sup> The process of claim 53, wherein  $R^4$  or  $R_5$  is carboxy, and wherein the compound of Formula (4) contains at least one chiral center.

<sup>53</sup>  
<sup>60</sup> The process of claim 53, wherein the compound of Formula (3) is attached to a solid support.

<sup>54</sup>  
<sup>61</sup> A free radical intermediate of the formula



wherein said fused aryl and/or heterocyclic ring possesses an  $sp^2$  hybridized carbon radical alpha to its point of attachment, and

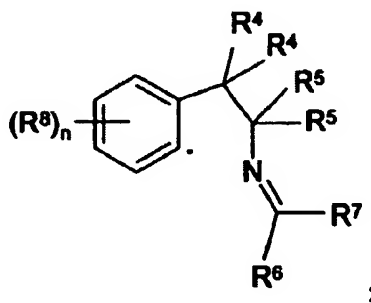
wherein each of the groups  $R^4$ ,  $R^5$ , and  $R^8$  are independently selected from hydrogen, aryl; heteroaryl; hydrocarbyl; substituted aryl; substituted heteroaryl; substituted hydrocarbyl; heteroatom connected aryl; heteroatom connected hydrocarbyl; heteroatom connected substituted hydrocarbyl; heteroatom connected heteroaryl; heteroatom connected substituted aryl; halo; amino; cyano; hydroxy; carboxy; a group of the formula  $-C(O)O-C_1-C_6$  alkyl; a group of the

formula  $-C(O)R^1$ ; a group of the formula  $-O-R^1$ ; a group of the formula  $-NHR^1$ ; a group of the formula  $-N(R^1)_2$ ;  $C_1-C_8$  alkoxy;  $C_1-C_8$  alkylthio; or two of  $R^5$  and  $R^6$ , or two  $R^8$  groups taken together can form a divalent hydrocarbyl, substituted hydrocarbyl, or be bonded directly to a heteroatom selected from oxygen, nitrogen, or sulfur; and n is a number equivalent to available sites on said aryl and/or heterocyclic ring;

in addition, two  $R^4$  groups and/or two  $R^5$  groups can be taken together represent oxo;

$R^6$  and  $R^7$  are independently selected from aryl, heteroaryl, hydrocarbyl, substituted aryl, substituted heteroaryl, and substituted hydrocarbyl; provided that said groups are bonded via a carbon atom.

55  
~~62~~: A free radical intermediate of the Formula  
 A



wherein each of the groups  $R^4$ ,  $R^5$ , and  $R^8$  are independently selected from hydrogen, aryl; heteroaryl; hydrocarbyl; substituted aryl; substituted heteroaryl; substituted hydrocarbyl; heteroatom connected aryl; heteroatom connected hydrocarbyl; heteroatom connected substituted hydrocarbyl; heteroatom connected heteroaryl; heteroatom connected substituted aryl; halo; amino; cyano; hydroxy; carboxy; a group of the formula  $-C(O)O-C_1-C_8$  alkyl; a group of the formula  $-C(O)R^1$ ; a group of the formula  $-O-R^1$ ; a group of the formula  $-NHR^1$ ; a group of the formula  $-N(R^1)_2$ ;  $C_1-C_8$  alkoxy;  $C_1-C_8$  alkylthio; or two of  $R^5$  and  $R^6$ , or two  $R^8$  groups taken together can form a divalent hydrocarbyl, substituted hydrocarbyl, or be bonded directly to a heteroatom selected from oxygen, nitrogen, or sulfur;

in addition, two  $R^4$  groups and/or two  $R^5$  groups can be taken together represent oxo;

$R^6$  and  $R^7$  are independently selected from aryl, heteroaryl, hydrocarbyl, substituted aryl, substituted heteroaryl, and substituted hydrocarbyl; provided that said groups are bonded via a carbon atom;

and n is from 0 to 4.

<sup>56</sup>  
~~63~~<sup>56</sup>. The intermediate of claim 62, wherein  $R^6$  and  $R^7$  are independently selected from  $C_1$ - $C_8$  alkyl, trifluormethyl, and phenyl.

<sup>57</sup>  
~~64~~<sup>57</sup>. The process of claim 1, wherein the process is conducted on a substrate which is enantiomerically enriched.

<sup>58</sup>  
~~65~~<sup>58</sup>. The process of claim 10, wherein the process is conducted on a substrate which is enantiomerically enriched.

<sup>59</sup>  
~~66~~<sup>59</sup>. The process of claim 17, wherein the process is conducted on a substrate which is enantiomerically enriched.

<sup>60</sup>  
~~67~~<sup>60</sup>. The process of claim 24, wherein the process is conducted on a substrate which is enantiomerically enriched.

<sup>61</sup>  
~~68~~<sup>61</sup>. The process of claim 32, wherein the process is conducted on a substrate which is enantiomerically enriched.

<sup>62</sup>  
~~69~~<sup>62</sup>. The process of claim 43, wherein the process is conducted on a substrate which is enantiomerically enriched.

<sup>63</sup>  
~~70~~<sup>63</sup>. The process of claim 49, wherein the process is conducted on a substrate which is enantiomerically enriched.

<sup>64</sup>  
~~71~~<sup>64</sup>. The process of claim 53, wherein the process is conducted on a substrate which is enantiomerically enriched.

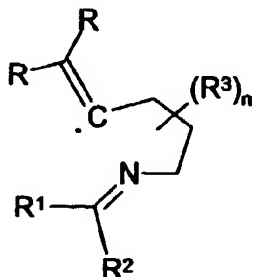


## Amendments to the Claims:

This listing of claims will replace all prior versions and listing of claims in the application.

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72. A free radical intermediate of the Formula

$$\Lambda$$


wherein each R is independently selected from the group consisting of hydrogen, hydrocarbyl, substituted hydrocarbyl, aryl, heteroaryl, substituted aryl, substituted heteroaryl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, heteroatom connected aryl, heteroatom connected heteroaryl, heteroatom connected substituted aryl, heteroatom connected substituted heteroaryl, a group of the formula  $-C(O)R^1$ , a group of the formula  $-O-R^1$ , a group of the formula  $-NHR^1$ , a group of the formula  $-N(R^1)_2$ , a group of the formula  $-Sn(R^1)_3$ , and a group of the formula  $-Si(R^1)_3$ ;

wherein the  $R^1$  and  $R^2$  groups are independently selected from the group consisting of aryl, heteroaryl, hydrocarbyl, substituted aryl, substituted heteroaryl, and substituted hydrocarbyl; provided that said groups are bonded via a carbon atom;

each  $R^3$  is independently selected from aryl; heteroaryl; hydrocarbyl; substituted aryl; substituted heteroaryl; substituted hydrocarbyl; heteroatom connected aryl; heteroatom connected hydrocarbyl; heteroatom connected substituted hydrocarbyl; heteroatom

connected heteroaryl; heteroatom connected substituted aryl; amino; halo; cyano; hydroxy; carboxy; a group of the formula  $-C(O)O-C_1-C_8$  alkyl; a group of the formula  $-C(O)R^1$ ; a group of the formula  $-O-R^1$ ; a group of the formula  $-NHR^1$ ; a group of the formula  $-N(R^1)_2$ ;  $C_1-C_8$  alkoxy;  $C_1-C_8$  alkylthio; and oxo; or two  $R^3$  groups taken together can form a divalent hydrocarbyl, substituted hydrocarbyl, or be bonded directly to a heteroatom selected from oxygen, nitrogen, or sulfur; and n is from 0 to 6.

66

73. The intermediate of claim 72, wherein  $R^1$  and  $R^2$  are selected from phenyl, trifluoromethyl, and  $C_1-C_8$  alkyl.

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74. The intermediate of claim 72, wherein n is 0.

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75. The intermediate of claim 72, wherein  $R^3$  is fluoro.